

APPENDIX H

**STATISTICAL AND GEOCHEMICAL EVALUATIONS
OF SITE METALS DATA**

Geochemical Evaluation of Metals in Soil, Sediment, Groundwater, and Surface Water at the Ranges West of Iron Mountain Road, Fort McClellan, Alabama

1.0 Introduction

This report provides the results of a geochemical evaluation of surface soil, sediment, groundwater, and surface water samples from the Ranges West of Iron Mountain Road, Fort McClellan, Calhoun County, Alabama. Twelve elements in soil, three elements in sediment, four elements in groundwater, and one element in surface water failed statistical comparison to background. A geochemical evaluation was performed to determine if the elevated concentrations are naturally occurring or if they contain a component of contamination.

Site samples included in the evaluations consist of 101 surface soil samples (0 to 1 foot below ground surface [bgs] or 0 to 2 feet bgs) collected from December 2000 to April 2001; 94 subsurface soil samples (various depths ranging from 2 to 12 feet bgs) collected in December 2002 to April 2001; 18 sediment samples collected in February and March 2001; 59 unfiltered groundwater samples collected from April 2001 to September 2002; and 18 unfiltered surface water samples collected in February and March 2001. All of the soil, sediment, and surface water samples were analyzed for the full list of 23 target analyte list (TAL) metals. Fifty-three of the groundwater samples were analyzed for TAL metals, and 6 of the groundwater samples were analyzed only for antimony. Installation-wide background data for TAL metals in soil, sediment, groundwater, and surface water are provided in the background study report (Science Applications International Corporation, 1998) and are used in the following evaluations.

2.0 Geochemical Evaluation Methodology

If an analyte fails statistical comparison to background as described in the “Statistical Comparison of Site and Background Data for Ranges West of Iron Mountain Road,” then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The importance of geochemical evaluations in distinguishing between site and background data sets has been recognized in the industry (EPA, 1995; Barclift, *et al.*, 2000; U.S. Navy, 2002; Myers and Thorbjornsen, 2004). When properly evaluated, geochemistry can provide mechanistic explanations for apparently high, yet naturally occurring, constituents. Anomalous samples that may represent contamination can also be readily distinguished from

uncontaminated samples. This section describes the geochemical evaluation techniques that were employed in the site-to-background comparisons.

2.1 Soil and Sediment

The geochemical evaluation is based on the natural associations of trace elements with specific minerals in the soil or sediment matrix. As an example, arsenic in most uncontaminated oxic soils is almost exclusively associated with iron oxide minerals (Bowell, 1994; Schiff and Weisberg, 1997). (The term “iron oxide” is used here to include oxides, hydroxides, oxyhydroxides, and hydrous oxides of iron.) This association of arsenic with iron oxides is a result of the adsorptive behavior of this particular trace metal in an oxic soil environment. Arsenic is present in oxic soil pore fluid as negatively charged oxyanions (HAsO_4^{-2} , H_2AsO_4^-) (Brookins, 1988). These anions have strong affinities to adsorb on the surfaces of iron oxides, which maintain a strong positive surface charge (Electric Power Research Institute [EPRI], 1986). If a soil sample has a high percentage of iron oxides, then it is expected to have a proportionally higher concentration of arsenic.

The absolute concentrations of arsenic and iron can vary by several orders of magnitude at a site, but the arsenic/iron ratios in the samples are usually quite constant as long as no contamination is present (Daskalakis and O'Connor, 1995). If a sample has some naturally occurring arsenic plus additional arsenic from an herbicide or some other source, then it will have an anomalously high ratio relative to the other uncontaminated samples. These ratios thus serve as a powerful technique for identifying contaminated samples.

The evaluation includes the generation of plots in which detected arsenic concentrations in a set of samples are plotted on the y-axis, and the corresponding detected iron concentrations are plotted on the x-axis. The slope of a best-fit line through the samples is equal to the average arsenic-to-iron background ratio. If the samples with the highest arsenic concentrations plot on the same linear trend as the other samples, then it is most probable that the elevated concentrations are natural, and are caused by the preferential enrichment of iron oxides in those samples. If the site samples with elevated arsenic concentrations plot above the trend displayed by the uncontaminated samples, then there is evidence that those samples have an excess contribution of arsenic, and contamination may be indicated.

Each trace element is associated with one or more minerals in the soil matrix. Vanadium and selenium, along with arsenic, form anionic species in solution and are associated with iron oxides, which maintain a positive surface charge. Divalent metals such as barium, cadmium,

lead, and zinc tend to form cationic species in solution and are attracted to clay mineral surfaces, which maintain a negative surface charge. These trace elements would be evaluated against aluminum, which is a major component of clay minerals. Manganese oxides also have an affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). These trace elements would be evaluated against manganese.

2.2 Groundwater and Surface Water

Elevated concentrations of inorganic constituents in groundwater and surface water samples may be due to naturally high dissolved concentrations, the presence of suspended particulates in the samples, reductive dissolution, or contamination resulting from site activities. This section discusses the major geochemical processes considered during the evaluation of groundwater and surface water analytical data.

Effects of Suspended Particulates. The presence of trace elements adsorbed on suspended particulates can greatly increase trace element concentrations as reported by an analytical laboratory. These adsorbed trace elements are not in true solution, and can be removed by settling or filtration. The same concepts involved in the evaluation of soil and sediment data also apply to groundwater and surface water data: samples containing trace elements adsorbed on suspended clay particulates should show a positive correlation with aluminum concentrations, and samples containing trace elements adsorbed on suspended iron oxides should show a positive correlation with iron concentrations. These correlations are evaluated by generating x-y plots of the concentrations of an elevated trace metal versus aluminum or iron (depending on the trace element).

The most common suspended particulates in groundwater samples are clay minerals; hydrous aluminum oxides ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) and hydroxides [$\text{Al}(\text{OH})_3$]; and iron oxide (Fe_2O_3), iron hydroxide [$\text{Fe}(\text{OH})_3$], and iron oxyhydroxide ($\text{FeO} \cdot \text{OH}$) minerals, collectively referred to as “iron oxides.” All clay minerals contain aluminum and have low solubilities over a neutral pH range of 6 to 8. Measured concentrations of aluminum in excess of ~1 milligram per liter (mg/L) indicate the presence of suspended clay minerals (Hem, 1985; Stumm and Morgan, 1996), with higher aluminum concentrations being a qualitative indicator of the mass of suspended clay minerals. Iron also has a very low solubility under neutral pH and moderate to oxidizing redox conditions, so that measured iron concentrations in excess of ~1 mg/L under these conditions indicate the presence of suspended iron oxides (Hem, 1985).

The presence of suspended clay or iron oxides in groundwater samples has particular importance in the interpretation of trace element concentrations. Most clay particles maintain a negative surface charge under neutral pH conditions, and have a strong tendency to adsorb positively charged (cationic) aqueous species. Iron oxides display the opposite behavior, maintaining a positive surface charge under neutral pH conditions, and have a strong tendency to adsorb negatively charged (anionic) aqueous species.

Barium, lead, and zinc are usually present in groundwater as divalent cations and thus tend to concentrate on clay surfaces (EPRI, 1984; Brookins, 1988). Arsenic, selenium, and vanadium are usually present under oxidizing conditions as oxyanions, and thus tend to concentrate on iron oxide surfaces (Bowell, 1994; Hem, 1985; Pourbaix, 1974; Brookins, 1988).

Chromium can be present in groundwater as a mixture of aqueous species with different charges, depending on pH (EPRI, 1984). The positive, neutral, and negative charges on these species result in the distribution of chromium on several different types of sorptive surfaces, including clay and iron oxide minerals.

As an example, the concentrations of zinc (y-axis) would be plotted against aluminum (x-axis). If all of the samples display a common linear trend, then it is most likely that the zinc concentrations are due to the presence of suspended clay minerals in the samples. The slope of a best-fit line through the points is equal to the average zinc/aluminum ratio. If some samples plot above the linear trend established by the other samples, then those samples have an anomalously high zinc/aluminum ratio, and most likely contain excess zinc that cannot be explained by these natural processes.

Alternative techniques for assessing the effects of suspended particulates on trace element concentrations are the evaluation of correlations of trace element concentrations versus turbidity, and comparison of analyses of filtered versus unfiltered splits of samples. Turbidity measurements are qualitative, and do not distinguish between suspended clay minerals, iron oxides, and natural organic material, so this approach lacks the resolution provided by trace element versus aluminum or trace element versus iron correlations.

If the concentrations of trace elements in unfiltered samples are correlated with aluminum or iron, then they are most likely adsorbed to the surfaces of suspended particulates. If these correlations are linear, then the elevated concentrations are most likely natural.

Effects of Reductive Dissolution. Iron and manganese oxides concentrate several trace elements such as arsenic, selenium, and vanadium on mineral surfaces, as discussed above. In soils and sedimentary aquifers, these elements are almost exclusively associated with iron and manganese oxide minerals and grain coatings, as long as the redox conditions are moderate to oxidizing.

The release of organic contaminants such as fuels or chlorinated solvents can establish local reducing environments caused by anaerobic microbial degradation of the organic compounds. The establishment of local reducing conditions can drive the dissolution of iron and manganese oxides, which become soluble as the redox potential drops below a threshold value. Dissolution of these oxide minerals can mobilize the trace elements that were adsorbed on the oxide surfaces, which is a process termed “reductive dissolution.” Several investigations have documented the mobilization of arsenic, selenium, and other trace elements under locally reducing redox conditions (Sullivan and Aller, 1996; Nickson, *et al.*, 2000; Belzile, *et al.*, 2000).

Evidence for reductive dissolution would be a correlation between elevated trace elements (arsenic, selenium, and vanadium in particular) versus lower redox conditions. Low redox conditions can be identified by local depressions in oxidation-reduction potential (ORP) or dissolved oxygen (DO) measurements, or the presence of reducing gases such as hydrogen, methane, ethane, or ethene. Anaerobic microbes can also reduce sulfate to sulfide and nitrate to ammonia, resulting in local depressions in sulfate and nitrate concentrations, and local detections of sulfide and ammonia. In areas impacted by chlorinated solvents, additional evidence for the establishment of anaerobic reducing conditions is the presence of *cis*-1,2-dichloroethene and/or vinyl chloride, which are reductive dechlorination products resulting from the microbial degradation of trichloroethene or tetrachloroethene under anaerobic conditions.

3.0 Results of the Geochemical Evaluation for Multiple Elements in Soil

This section presents the results of the geochemical evaluation of aluminum, antimony, arsenic, beryllium, cadmium, iron, magnesium, mercury, potassium, selenium, thallium, and zinc in the site soil samples. Correlation plots are provided in Attachment 1 of this report.

Aluminum

Aluminum is the second-most abundant of the 23 elements analyzed in the site soil samples, with a mean concentration of 9,062 mg/kg (0.9 weight percent). Aluminum is a naturally occurring element that is a primary component of soil-forming minerals such as clays, feldspars, and

micas; the site soil boring logs note the presence of clays in many of the sampled intervals. Iron oxides are minerals that are also common in soil. Clays and iron oxides tend to exist as very fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. A plot of aluminum versus iron concentrations can be used to qualitatively assess the relative abundance of these minerals in site soil (Figure 1). Site surface soil samples are represented by open triangles, site subsurface soil samples by filled triangles, and background soil samples by filled circles. The site samples exhibit a similar range of concentrations as the background samples and they lie on the general background trend, indicating that aluminum in the site samples is naturally occurring. It is worth noting that iron oxide and clay minerals adsorb specific trace elements (as discussed in Section 2.1), so samples that plot on the upper end of the trend in Figure 1 are expected to contain proportionally higher concentrations of trace elements.

Conclusion

Aluminum detected in the site soil samples is naturally occurring.

Antimony

Antimony has an affinity to adsorb on clays and iron oxides (Kabata-Pendias, 2001), so positive correlations between antimony versus aluminum and antimony versus iron are expected for uncontaminated samples. The background samples form a linear trend with a positive slope in a plot of antimony versus iron (Figure 2). The site samples all lie above the background trend, but they form a linear trend with a shallow positive slope. This linearity represents a consistent Sb/Fe ratio that would not be expected if the source of the antimony was site-related contamination. It should be noted that the site reporting limits, which range from 10 to 18.3 mg/kg, are significantly higher than the background reporting limits, most of which are in the 0.079 to 1 mg/kg range. Furthermore, all of the site detections are estimated ("J"-qualified) values below the reporting limit, and there is a high degree of uncertainty surrounding such measurements. These differences in reporting limits, and the prevalence of estimated concentrations in the site data set, likely explain the different Sb/Fe ratios observed between the site and background data sets.

Conclusion

Antimony detected in the site soil samples is most likely naturally occurring.

Arsenic

As discussed in Section 2.1, arsenic in oxic soils has a strong affinity to adsorb on iron oxides. A positive correlation between arsenic and iron is expected for uncontaminated samples under those conditions. A plot of arsenic versus iron reveals a common linear trend with a positive slope for the site and background samples (Figure 3). The site samples with high arsenic concentrations also contain proportionally higher iron, and lie on the linear trend. These observations indicate that arsenic in the site samples is associated with iron oxides at a relatively constant ratio, and is natural. One exception is subsurface soil sample JM0004 (0.718 J mg/kg As), which lies below the linear trend. This sample contains a relatively low As/Fe ratio, but its arsenic concentration is well within the background range.

Conclusion

Arsenic concentrations detected in the site soil samples are naturally occurring.

Beryllium

Beryllium concentrations in soil are commonly controlled through adsorption on iron oxides (Vesely, *et al.*, 2002), so a positive correlation between beryllium and iron would be expected for uncontaminated samples. A plot of beryllium versus iron is provided in Figure 4. The site and background samples form a common linear trend, and the site samples that have high beryllium concentrations also have high iron. These observations indicate a natural source for beryllium in the site samples.

Conclusion

Beryllium detected in the site soil samples is naturally occurring.

Cadmium

Cadmium is commonly present in soils as a divalent cation, and has an affinity to adsorb on manganese oxides (Kabata-Pendias, 2001). A positive correlation between cadmium and manganese is thus expected in uncontaminated soils. A plot of cadmium versus manganese is provided in Figure 5. The background samples form a generally linear trend with a positive slope, and one of the two site samples with detectable cadmium lies on the background trend. Cadmium in these samples is naturally occurring. Surface soil sample JP0003 (from sample location HR-151Q-GP01), however, has the highest cadmium concentration (4.37 mg/kg) of the site and background data sets but only moderate manganese, and lies above the trend formed by the other samples. Elevated cadmium in this sample is unexpected, and should be considered suspect.

Conclusion

The cadmium concentration in surface soil sample JP0003 is anomalously high and may contain a component of contamination.

Iron

Iron is the most abundant of the 23 elements analyzed in the site soil samples, with a mean concentration of 19,393 mg/kg (1.9 weight percent). As discussed in the Aluminum evaluation, iron oxides and clays are common soil-forming minerals. A plot of aluminum versus iron concentrations provides a qualitative indicator of the relative abundance of these minerals in site soil (Figure 1). The site samples exhibit a slightly broader range of iron concentrations than the background samples, but they all lie on the general background trend. Iron in the site samples is most likely present in the form of iron oxides, and is naturally occurring. It is important to note that iron oxides and clays adsorb specific trace elements (as discussed in Section 2.1), so samples that plot on the upper end of the trend in Figure 1 are expected to contain proportionally higher concentrations of trace elements.

Conclusion

Iron detected in the site soil samples is naturally occurring.

Magnesium

Calcium and magnesium have similar chemical properties, and magnesium often substitutes for calcium in minerals. A plot of magnesium versus calcium reveals a generally linear trend with a

positive slope for the site and background samples (Figure 6). The site samples with the highest magnesium concentrations also contain the highest calcium, and lie on the linear trend. Magnesium in the site samples is naturally occurring.

Conclusion

Magnesium detected in the site soil samples is naturally occurring.

Mercury

Mercury can adsorb onto clays and iron oxides in soil, but its concentrations are also commonly controlled through organic complex formation (Kabata-Pendias, 2001). As a result, poor correlations between mercury and aluminum or mercury and iron are often observed, even in uncontaminated soil samples. The site samples lie on the general background trend in a plot of mercury versus aluminum (Figure 7). The site sample with the highest mercury concentration (JT0002; 0.27 mg/kg Hg) also has the highest aluminum concentration of the site and background data sets, indicating that this sample is enriched in clays and associated trace elements. Mercury in the site samples is most likely natural.

Conclusion

Mercury concentrations detected in the site soil samples are most likely naturally occurring.

Potassium

Potassium is a major element that is a common constituent of minerals such as clays and feldspars, which also contain aluminum. A plot of potassium versus aluminum is provided in Figure 8. The site surface soil samples with high potassium also have high aluminum, indicating that these samples are preferentially enriched in clays (and other aluminum-bearing minerals) and that the potassium is natural. Some of the subsurface soil samples contain high potassium but only moderate aluminum, and lie above the trend formed by the other site samples. However, there are several background samples with similarly high K/Al ratios. These samples most likely reflect the natural variability in K/Al ratios in Ft. McClellan soils.

Conclusion

Potassium detected in the site soil samples is naturally occurring.

Selenium

As explained in Section 2.1, selenium has a strong affinity to adsorb on iron oxides in oxic soils, so a positive correlation between selenium and iron is expected for uncontaminated soil samples. Comparison to background is hindered because of the high percentage of nondetects in the background data set. However, a plot of selenium versus iron reveals a generally linear trend with a positive slope for most of the site samples, and the two background samples with detectable selenium lie on this trend (Figure 9). Most of the site samples with high selenium also exhibit high iron, and lie on the linear trend. These observations indicate that selenium in these samples is associated with iron oxides at a relatively constant ratio, and is natural. Subsurface soil sample ECC0044 (from sample location HR-232QX-GP02; 9 to 12 feet bgs), however, has the highest selenium concentration of the site and background data sets (2.81 mg/kg) but only moderate iron (as well as moderate aluminum and low manganese), and lies above the trend formed by the other samples. Elevated selenium in this sample is unexpected, and should be

considered suspect. It is important to note that this result is an estimated concentration; there is a high degree of uncertainty associated with such values, and that may explain the anomalously high Se/Fe ratio.

Conclusion

The selenium concentration detected in subsurface soil sample ECC0044 is anomalously high relative to the major element concentrations and should be considered suspect.

Thallium

Weak correlations between thallium concentrations versus major element concentrations are commonly observed in soil data sets, even in uncontaminated samples. This may be explained at least in part by the presence of low estimated (“J”-qualified) values below the reporting limit, values that commonly characterize thallium analyses in uncontaminated samples. The background samples exhibit poor correlation ($R^2 = 0.025$) in a plot of thallium versus iron (Figure 10). The site samples all lie slightly above the general background trend, but they form a linear trend with a shallow positive slope ($R^2 = 0.23$ and 0.35 for the surface and subsurface intervals). This linearity represents a consistent Tl/Fe ratio that would not be expected if the source of the thallium was site-related contamination. It should be noted that the site reporting limits, which range from 2 to 3.66 mg/kg, are higher than most of the background reporting limits. Furthermore, most of the site detections are estimated (“J”-qualified) values below the reporting limit, and there is a high degree of uncertainty surrounding such measurements. These differences in reporting limits, and the prevalence of estimated concentrations in the site data set, likely explain the difference in Tl/Fe ratios observed between the site and background data sets. It is also important to note that the site concentrations are well below the background maximum of 23.5 mg/kg.

Conclusion

Thallium concentrations detected in the site soil samples are most likely naturally occurring.

Zinc

Zinc in soil has an affinity for multiple sorptive surfaces, including clays, iron oxides, and manganese oxides, and it can also substitute for magnesium in silicate minerals (Kabata-Pendias, 2001). Plots of zinc versus iron and zinc versus manganese are provided in Figures 11a and 11b. All of the site surface soil samples lie on the linear background trend in Figure 11b, and the surface soil samples with the highest zinc also contain proportionally higher manganese. These observations indicate that zinc in the surface soil samples is associated with manganese oxides at a relatively constant ratio, and is natural. Several site subsurface samples lie slightly above the background trend in Figure 11b, but they all lie on the linear background trend in Figure 11a. Elevated zinc in the subsurface soil samples is observed in samples with proportionally higher iron. This indicates that zinc in the subsurface soil samples is associated with iron oxides at a relatively constant ratio, and is natural.

Conclusion

Zinc concentrations detected in the site soil samples are naturally occurring.

4.0 Results of the Geochemical Evaluation for Multiple Elements in Sediment

This section presents the results of the geochemical evaluation of aluminum, cadmium, and mercury in the site sediment samples. Correlation plots are provided in Attachment 1.

Aluminum

Aluminum is a primary component of common minerals such as clays, feldspars, and micas. Iron oxides are minerals that are also common in sediment. Clays and iron oxides tend to exist as very fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. A plot of aluminum versus iron concentrations can be used to qualitatively assess the relative abundance of these minerals in site sediment (Figure 12). The site samples exhibit higher aluminum concentrations than many of the background samples, but they lie on the linear background trend. This suggests that the site samples are naturally enriched in clays relative to most of the background samples, and that the aluminum is natural. It is worth noting that iron oxide and clay minerals adsorb specific trace elements (as discussed in Section 2.2), so samples that plot on the upper end of the trend in Figure 12 are expected to contain proportionally higher concentrations of trace elements.

Conclusion

Aluminum detected in the site sediment samples is naturally occurring.

Cadmium

Cadmium has an affinity to adsorb on clays (Kabata-Pendias, 2001), so a positive correlation between cadmium and aluminum is expected for uncontaminated samples. The background samples form a weak linear trend with a positive slope in plot of cadmium versus aluminum (Figure 13). The two site samples with detectable cadmium have high cadmium relative to many of the background samples, but they also contain proportionally higher aluminum and lie on the background trend. This suggests a natural source for cadmium in the site samples.

Conclusion

Cadmium detected in the site sediment samples is naturally occurring.

Mercury

Mercury concentrations in sediment are commonly controlled through organic complex formation (Kabata-Pendias, 2001), so poor correlations between mercury and iron or mercury and aluminum are often observed, even in uncontaminated soil samples. A plot of mercury versus aluminum is provided in Figure 14. Most of the site samples lie on the linear trend established by the background samples, indicating that the mercury in these samples is associated with clays at ratios consistent with those of the background samples. A few samples lie slightly below the background trend, but their mercury concentrations are well within the background range. Mercury detected in the site samples is naturally occurring.

Conclusion

Mercury detected in the site sediment samples is naturally occurring.

5.0 Results of the Geochemical Evaluation for Multiple Elements in Groundwater

This section presents the results of the geochemical evaluation of antimony, beryllium, chromium, and nickel in unfiltered groundwater samples from the Ranges West of Iron Mountain Road. Correlation plots are provided in Attachment 1.

Field-measured pH readings for the site groundwater samples range from 3.7 to 8.78 standard units, with a mean of 5.35 and median of 5.13. These observations indicate a wide range of pH conditions at the sample locations, ranging from acidic to slightly alkaline. Field-measured DO readings range from 0.21 to 14.33 mg/L, with a mean of 6.84 mg/L and median of 7.03 mg/L, and ORP readings range from -78 to +421 millivolts (mV), with a mean of +244 mV and median of +274 mV. These readings indicate oxidizing redox conditions at most of the sample locations, with slightly reducing conditions at some locations. Turbidity measurements range from 1.2 to 1000 nephelometric turbidity units (NTU), with a mean of 130 NTUs and median of 10.6 NTU. These values suggest that several samples contained a significant mass of suspended particulates.

Antimony

Comparison to background is hindered by the high percentage of nondetects in the background data set. A plot of detected antimony concentrations versus detected iron concentrations is provided in Figure 15. The site samples form a linear trend with a positive slope, indicating that antimony in the site samples is associated with suspended iron oxides at a relatively constant ratio, and is natural. It is important to note that the two background detections are several orders of magnitude below their reporting limit of 0.1 mg/L; the antimony in these two samples may be in solution, which would explain their low Sb/Fe ratios.

Conclusion

Antimony concentrations detected in the site samples are naturally occurring.

Beryllium

Beryllium has a strong affinity to adsorb on clays (EPRI, 1984), so a positive correlation between beryllium and aluminum is expected for uncontaminated samples under natural groundwater conditions. The background samples form a generally linear trend in a plot of beryllium versus aluminum (Figure 16). Two of the site samples lie on this trend, indicating that beryllium in these samples is associated with suspended clay minerals at ratios consistent with background, and is natural. Sample JM3007, however, contains the highest beryllium concentration of the two data sets (0.00512 mg/L) but only moderate aluminum, and lies above

the background trend. There may be a component of contamination in this sample, which was collected from monitoring well HR-117Q-MW07 on 05/11/01.

Conclusion

The beryllium concentration detected in sample JM3007 is anomalously high and may contain a component of contamination.

Chromium

As noted in Section 2.2, chromium can be present in groundwater as a mixture of aqueous species with different charges, depending on pH, and thus chromium can have an affinity for several different types of sorptive surfaces, including clay and iron oxide minerals. A plot of chromium versus aluminum is provided in Figure 17. Comparison to background is precluded by the high percentage of nondetects in the background data set (100 percent). However, the site samples exhibit a linear trend with a positive slope, and the site sample with the highest chromium concentration also contains the highest aluminum. Chromium detected in the site samples is associated with suspended clay particulates at a relatively constant ratio, and is natural.

Conclusion

Chromium detected in the site groundwater samples is naturally occurring.

Nickel

Comparison to background is hindered by the high percentage of nondetects in the background data set. However, a plot of nickel versus aluminum reveals a linear trend with a positive slope for the site samples (Figure 18). Site sample ECC3016 contains the highest nickel concentration (0.0408 mg/L) but it also contains the highest aluminum concentration of the site samples (3.71 mg/L), and lies on the trend formed by the other samples. These observations indicate that nickel in the site samples is associated with suspended clays at a relatively constant ratio, and is natural.

Conclusion

Nickel detected in the site groundwater samples is naturally occurring

6.0 Results of the Geochemical Evaluation for Arsenic in Surface Water

This section presents the results of the geochemical evaluation of arsenic in unfiltered surface water samples from the Ranges West of Iron Mountain Road. The corresponding correlation plot is provided in Attachment 1.

Field-measured pH readings range from 4.32 to 6.01 standard units, with a mean of 4.99 and median of 4.82. These observations indicate slightly acidic pH conditions at most of the sample locations. Field-measured DO readings for these samples range from 1.5 to 8.19 mg/L, with a

mean of 5.37 mg/L and median of 5.69 mg/L, and the available ORP readings (for 50 percent of the samples) range from +195 to +295 mV, with a mean of +242 mV and median of +240 mV. These readings suggest oxidizing conditions in the surface water at the time of sample collection. Turbidity measurements range from 0 to 346 NTUs, with a mean of 23 NTUs and median of 0 NTU. These values suggest that most samples did not contain a significant mass of suspended particulates.

Arsenic

Arsenic was detected in 2 of the 18 unfiltered surface water samples (JL2001 and ECC2003). As discussed previously, under natural conditions arsenic is present in waters primarily as oxyanions and its concentrations are often controlled by adsorption on iron oxides. DO readings for samples JL2001 and ECC2003 are 5.04 mg/L and 8.19 mg/L, respectively, and the ORP measurement for sample JL2001 is +210 mV; these values indicate oxidizing conditions at the time of sample collection. Arsenic in these samples is thus expected to be present primarily as arsenate, which has a strong affinity to adsorb on suspended iron oxides. A plot of detected arsenic concentrations versus detected iron concentrations is provided in Figure 19. The background samples form a linear trend with a shallow positive slope, and the two site samples lie on this trend. Site sample ECC2003 contains the higher detected arsenic concentration (0.00545 J mg/L As) of the two site samples, but it also contains the highest iron (11.6 mg/L) and highest aluminum (9.71 mg/L) in the site data set, as well as the highest turbidity (346 NTUs). These observations indicate that some or most of the arsenic observed in the site samples is associated with suspended iron oxides (at a relatively constant ratio), and is natural.

Conclusion

Arsenic concentrations detected in the site surface water samples are naturally occurring.

7.0 Summary

This section summarizes the results of the geochemical evaluations of selected inorganics in surface soil, sediment, groundwater, and surface water samples from the Ranges West of Iron Mountain Road.

Soil. Geochemical evaluation indicates that all of the aluminum, antimony, arsenic, beryllium, iron, magnesium, mercury, potassium, thallium, and zinc concentrations detected in the surface and subsurface soil samples are naturally occurring. Surface soil sample JP0003 (from sample location HR-151Q-GP01) contains an anomalously high concentration of cadmium, and subsurface soil sample ECC0044 (HR-232QX-GP02) contains an anomalously high concentration of selenium; these two elevated concentrations may contain a component of contamination.

Sediment. Geochemical evaluation indicates that detected concentrations of aluminum, cadmium, and mercury in the surface soil samples are naturally occurring.

Groundwater. Geochemical evaluation indicates that antimony, chromium, and nickel concentrations detected in the unfiltered groundwater samples are naturally occurring. The beryllium concentration in sample JM3007 (collected from monitoring well HR-117Q-MW07 on 05/11/01) is anomalously high and may contain a component of contamination.

Surface Water. Geochemical evaluation indicates that arsenic concentrations detected in the surface water samples are naturally occurring.

8.0 References

Barclift, D., J. Heath, and A. Drucker, 2000, "Focus on Environmental Background Data Analysis," *Soil Sediment & Groundwater*, August/September, pp. 10-17.

Belzile, N., Y. W. Chen, and R. Xu, 2000, "Early Diagenetic Behavior of Selenium in Freshwater Sediments," *Applied Geochemistry*, Vol. 15, pp. 1439-1454.

Bowell, R. J., 1994, "Sorption of Arsenic by Iron Oxides and Oxyhydroxides in Soils," *Applied Geochemistry*, Vol. 9, pp. 279-286.

Brookins, D. G., 1988, *Eh-pH Diagrams for Geochemistry*, Springer-Verlag.

Cornell, R. M. and U. Schwertmann, 1996, *The Iron Oxides: Structure, Properties, Reactions, Occurrence, and Uses*, VCH, Weinheim.

Daskalakis, K. D. and T. P. O'Connor, 1995, "Normalization and Elemental Sediment Contamination in the Coastal United States," *Environmental Science & Technology*, Vol. 29, No. 2, pp. 470-477.

Electric Power Research Institute (EPRI), 1984, *Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, Volume 1: A Critical Review*, EPRI EA-3356, Palo Alto, California.

Electric Power Research Institute (EPRI), 1986, *Speciation of Selenium and Arsenic in Natural Waters and Sediments, Volume 2: Arsenic Speciation*, EPRI EA-4641, Palo Alto, California.

Hem, J. D., 1985, *Study and Interpretation of the Chemical Characteristics of Natural Water*, U. S. Geological Survey, Water Supply Paper 2254, 3rd Edition.

Kabata-Pendias, A., 2001, *Trace Elements in Soils and Plants*, Third Edition, CRC Press.

Myers, J. and K. Thorbjornsen, 2004, "Identifying Metals Contamination in Soil: A Geochemical Approach," *Soil & Sediment Contamination: an International Journal*, Vol. 13, No. 1 (in press).

Nickson, R. T., J. M. McArthur, P. Ravenscroft, W. G. Burgess, and K. M. Ahmed, 2000, "Mechanism of Arsenic Release to Groundwater, Bangladesh and West Bengal," *Applied Geochemistry*, Vol. 15, pp. 403-413.

Pourbaix, 1974, *Atlas of Electrochemical Equilibria in Solutions*, National Association of Corrosion Engineers, Houston, Texas.

Science Applications International Corporation, 1998, *Final Background Metals Survey Report, Fort McClellan, Anniston, Alabama*, July.

Schiff, K. and S. B. Weisberg, 1997, "Iron as a Reference Element for Determining Trace Metal Enrichment in California Coastal Shelf Sediments," in: S. Weisberg, C. Francisco, and D. Hallock, (eds.), *Southern California Coastal Water Research Project Annual Report 1995-96*, pp. 68-78.

Stumm, W. and J. Morgan, 1996, *Aquatic Chemistry*, Third Edition, Wiley-Interscience, New York.

Sullivan, K. A. and R. C. Aller, 1996, "Diagenetic Cycling of Arsenic in Amazon Shelf Sediments," *Geochimica et Cosmochimica Acta*, Vol. 60, No. 9, pp. 1465-1477.

U.S. Environmental Protection Agency (EPA), 1995, *Determination of Background Concentrations of Inorganics in Soils and Sediments at Hazardous Waste Sites*, Office of Research and Development, EPA/540/S-96/500, December.

U.S. Navy, 2002, *Guidance for Environmental Background Analysis, Volume 1: Soil*, NFESC User's Guide UG-2049-ENV, Naval Facilities Engineering Command, Washington, D.C., April.

Vesely, J., S. A. Norton, P. Skrivan, V. Majer, P. Kram, T. Navratil, and J. M. Kaste, 2002, "Environmental Chemistry of Beryllium," in: Grew, E. S. (ed.), *Reviews in Mineralogy and Geochemistry, Volume 50, Beryllium: Mineralogy, Petrology, and Geochemistry*, Mineralogical Society of America, Washington, D.C.

ATTACHMENT 1





















